**Catalyst Selectivity in Hydrocarbon Reactions: Ethylene on Ru/SiO$_2$ and M-Ru/SiO$_2$**

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The nuclear spin dynamics of $^1$H in adsorbed hydrogen, and $^{13}$C in adsorbed ethylene on Ru/SiO$_2$ and M-Ru/SiO$_2$ (M=Cu,Ag or Au) catalysts are used to probe surface concentrations of Ru and M, reactive intermediates, and selectivity in hydrocarbon conversion reactions. The temperature and exposure dependence of ethylene reaction on Ru/SiO$_2$ is investigated via various $^{13}$C NMR techniques, as well as via $^1$H multiple quantum coherence. Comparisons between monometallic and bimetallic catalysts are made.

Introduction.
Solid state NMR is becoming an increasingly important tool in the study of heterogeneous catalysis. The ability to directly study phenomena on the surfaces of dispersed metal particles is one advantage offered by NMR. This is contrasted with mainstay ultrahigh vacuum techniques requiring single crystal surfaces, which may not always be good models for real catalysts. The objective of this paper is to demonstrate the application of several solid state NMR techniques to study the fundamental processes associated with hydrocarbon conversion over supported bimetallic catalysts. To this end, the interaction of hydrogen with M-Ru/SiO$_2$ (M=Cu,Ag or Au) is used to probe catalyst surface composition. An investigation of ethylene reaction on mono- and bimetallic catalysts at various temperatures, exposures and M composition is presented.

Experimental.
Catalyst samples were prepared as described previously.[1],[2] $^1$H NMR was performed on a 220 MHz homebuilt spectrometer, equipped with an 8-bit digital phase shifter.[3] Multiple quantum coherence was developed using a single quantum propagator.[4] $^{13}$C NMR experiments were carried out on another homebuilt spectrometer operating at 100.06 MHz for $^1$H and 25.16 MHz for $^{13}$C. Transient techniques included cross polarization (CP) and direct excitation (Bloch decay), both of which were done with and without magic angle spinning (MAS) and proton decoupling. Special procedures were developed for low temperature (85-300K) experiments whereby samples were prepared, sealed, transferred to the spectrometer, and measured using CP/MAS without rise in temperature at any time.[5]

Results and Discussion.
NMR of Adsorbed Hydrogen: Establishing the Surface Composition of Bimetallic Catalysts
Studies on Cu-Ru/SiO$_2$ have shown that, at room temperature, hydrogen undergoes fast exchange between the two metals such that the observed lineshift, $\delta_{obs}$, may be expressed as:
$$\delta_{obs} = X_{Ru}\delta_{Ru} + X_{Cu}\delta_{Cu/Ru},$$
where $X_i$ is the surface concentration of metal i, $\delta_{Ru}$ and $\delta_{Cu/Ru}$ are the lineshifts for hydrogen chemisorbed on Ru/SiO$_2$ and the asymptotic limit as $X_{Cu}$ approaches unity in Cu-Ru/SiO$_2$, respectively.[6] Thus, the surface composition of the bimetallic catalyst can be obtained from $^1$H spectra (Fig. 1).
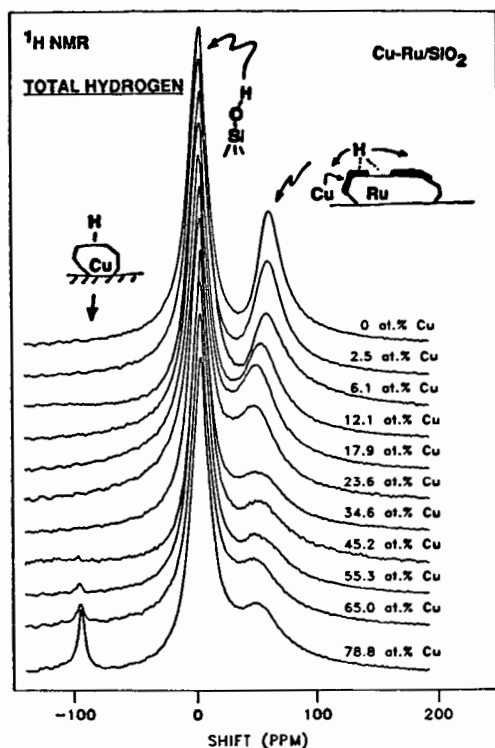
Fig. 1. NMR of adsorbed hydrogen on Cu-Ru/SiO₂ as a function of Cu concentration. The first moment of the upfield peak establishes the surface concentration of Ru.

Peak shifts in Fig. 1 demonstrate that $X_{Ru}$ decreases quickly as the total Cu concentration increases from 0 to 20 at.%, before levelling off at ca. 35 at.%, and approaches zero at ca. 80 at.%, where complete masking of Ru is concluded. These trends suggest that Cu forms a thin monoatomic layer on Ru particles, until near complete coverage, after which 3-d Cu islands and/or pure particles begin to form, as evidenced by the emergence of a downfield peak indicative of hydrogen chemisorbed on bulk Cu (cf. Figure 1). Hydrogen uptake and ^{1}H NMR studies on Ag-Ru/SiO₂ and Au-Ru/SiO₂ indicate a higher tendency for these metals to form three dimensional aggregates.[2]

NMR of Adsorbed Ethylene: Weakly and Strongly Adsorbed Intermediates and Products
Ethylene on Ru/SiO₂

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Transient NMR techniques were used to probe the development of intermediates and products as $^{13}C$-labelled ethylene reacted over $Ru/SiO_2$ to establish:

(i)     concentrations of weakly and strongly adsorbed species (Bloch decay),

(ii)    possible identities of strongly adsorbed intermediates (Bloch decay, CP/MAS, dipolar dephasing), and

(iii)   identities of weakly adsorbed products (liquid state NMR techniques).

Intensity measurements indicated that no significant amounts of $^{13}C$ nuclei remain undetected in the Bloch decay studies. Assignments of weakly adsorbed species could be made unambiguously based on chemical shifts, relative intensities of the various peaks, and, in some cases, J-splittings. These experiments were performed at a high magnetic field (300 MHz), using slow MAS to remove broadening due to magnetic susceptibility. The identification of strongly adsorbed species based solely on NMR shifts is not straightforward. Although MAS can remove the effect of anisotropies of chemical shift, Knight shift, and magnetic susceptibility, considerable line broadening often remains due to the distribution of sites across the metal particles. The extent to which isotropic Knight shifts affect the identification of $^{13}C$ resonances of hydrocarbon species on highly dispersed, supported Ru is debatable. Dipolar dephasing and multiple quantum NMR were also used to probe possible identities of the strongly adsorbed species.

Selectivity and product distributions are strong functions of temperature and surface coverage. Fig. 2 shows an example of the temperature dependence of $^{13}C$ CP/MAS spectra of ethylene dosed on $Ru/SiO_2$ at 78K. The exposures ($\epsilon$) were 0.5 and 1.5 ethylene molecules per surface Ru atom, and spectra were accumulated at 85K, at 185 K after reaction at that temperature for 2 days, and at 300 K after reaction at 300 K for 1 day.[7]
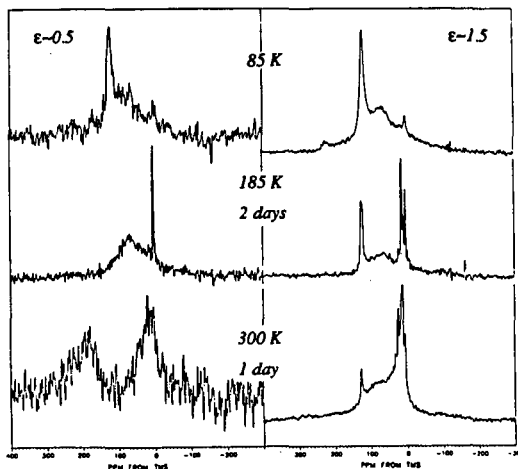


Fig. 2. NMR of $^{13}C$ in ethylene adsorbed on $Ru/SiO_2$ as a function of exposure ($\epsilon$ = 0.5 and 1.5), and temperature (85K$\leq$T$\leq$300K).

Both exposures give similar spectra at 85K. Peaks are assigned to weakly and strongly adsorbed ethylene, the strongly adsorbed species being either $\pi$, or di-$\sigma$ bonded to the metal surface. To distinguish between the $\pi$ and di-$\sigma$ bound species, bond length measurements may be performed using the homonuclear dipolar coupling between ^{13}C nuclei. This work is in progress.

At 185K and $\varepsilon = 0.5$, only ethane is observed in the weakly adsorbed layer. Changes in the spectrum also suggest a strongly bound $C_2H_2$ species in addition to the strongly bound $C_2H_4$. For $\varepsilon = 1.5$, the increase in temperature leads to the development of weakly bound cis- and trans-butenes.

At 300K, for $\varepsilon = 0.5$, broad peaks are observed at ca. 185 and 10 ppm, which are tentatively assigned to the >C- and -$CH_3$ carbons of ethylidyne, although experiments are underway to further investigate this assignment. At $\varepsilon = 1.5$, the weakly adsorbed species were identified as ethane, butenes, and butane. Surface attached alkyl groups and acetylide are inferred to be present in the strongly bound layer.[1]

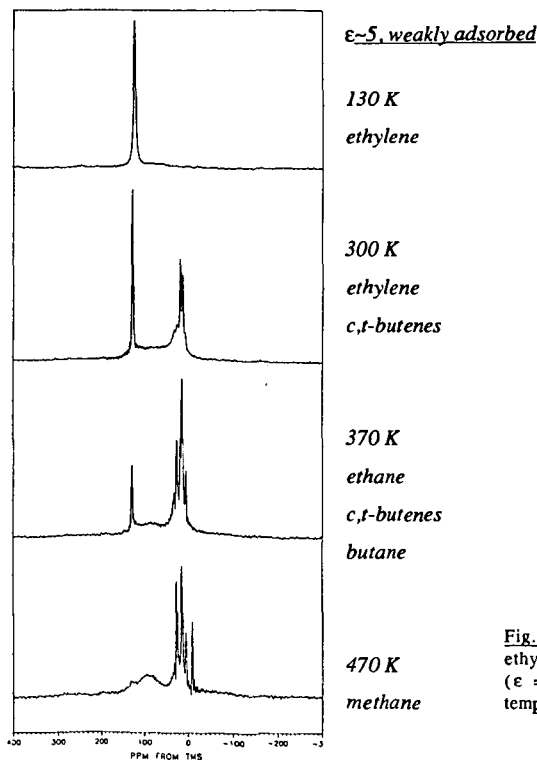Evolution of weakly adsorbed products is shown in Fig. 3, for an $\varepsilon = 5$ sample. At 140K,



*ε~5, weakly adsorbed*

130 K
*ethylene*

300 K
*ethylene*
*c,t-butenes*

370 K
*ethane*
*c,t-butenes*
*butane*

470 K
*methane*

Fig. 3. ^{13}C CP/MAS NMR of ethylene adsorbed on Ru/SiO$_2$ ($\varepsilon = 5$) as a function of temperature.

only ethylene is observed. When the temperature is raised to 300K, cis- and trans- butenes are formed. Butadiene is observed as a transient during this temperature rise. Increasing temperature to 370K results in the formation of ethane and butane. At 470K only the fully hydrogenated products, methane, ethane and butane, are observed. The appearance of methane indicates that C-C bond cleavage has already occurred at or below 470K.

As a means of further establishing identities of the strongly adsorbed species, multiple quantum spin counting was used.[4] Under the conditions imposed in this experiment for the development of multiple quantum coherence, the number of coupled spins is $k_{max} + 1$, where $k_{max}$ is the highest order of observed coherence. The silanol protons of the support, separated by ca. 4Å, only develop double quantum coherence in a period sufficient to see $k > 8$ for the infinitely coupled ensemble of spins in adamantane. Fig. 4 shows the multiple quantum spectrum of the strongly adsorbed species resulting from ethylene adsorption on Ru/SiO$_2$. $k_{max}$ sharply cuts off at a value of 5, indicating that species with no more than 6 strongly coupled protons are present in the sample. One possible candidate for the fragment with 6 coupled protons is metallocyclic (Ru)CH$_2$CH=CHCH$_2$(Ru), which may be a participant in the formation of butenes. Small concentrations of this species cannot be excluded on the basis of $^{13}$C NMR data.
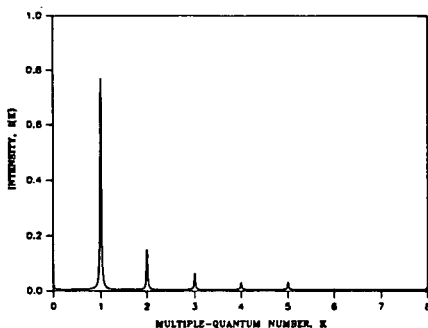


**Fig. 4.** Multiple quantum spectrum of strongly bound species from reaction of ethylene with Ru/SiO$_2$.

### Ethylene on M-Ru/SiO$_2$

Unlike the extensive reaction of ethylene on Ru/SiO$_2$, no reaction is observed on Cu/SiO$_2$ at 300K. The bimetallic Cu-Ru/SiO$_2$ differs from the monometallic Ru/SiO$_2$ in that the ability of the catalyst to produce hydrogenated products is reduced. At room temperature, the intermediate, butadiene, is stabilized in the bimetallic system.[8] This is evidenced by Fig. 5, which shows the CP/MAS spectrum of $^{13}$C in ethylene adsorbed on a 15 at. % Cu bimetallic catalyst.

Cu and Ru are known to be immiscible in the bulk.[9] Monte-Carlo simulations[10] indicate Cu-Ru bimetallic particles to be polyhedra in which the Cu selectively populates high coordination edge and corner sites, and then forms islands on the particle faces as Cu content increases. The equilibrium structure for a Cu-Ru particle with 15 at.% Cu, as predicted by Monte Carlo simulations, is shown in Fig. 5. It is therefore postulated that the selectivity towards highly

hydrogenated products is affected by the availability of edge and corner Ru sites, which become blocked by the adsorption of Cu.
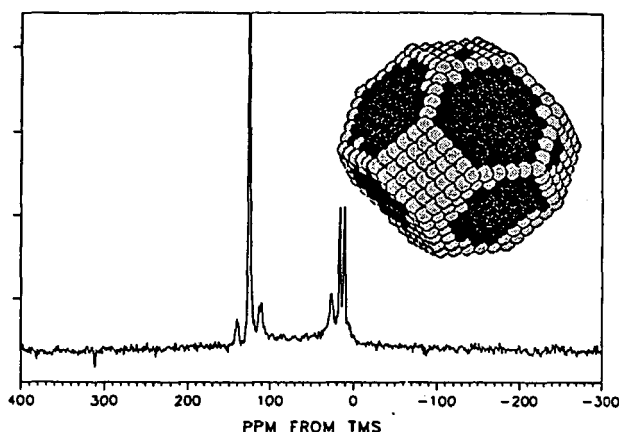


Fig. 5. NMR of $^{13}$C adsorbed on Cu-Ru/SiO$_2$ at room temperature. Total metal loading = 4%, Cu = 15% of total metal.

Ethylene reaction on Ag-Ru/SiO$_2$ shows reduced hydrogenation[2] as compared to Ru/SiO$_2$, but not as much as for Cu-Ru/SiO$_2$. Although Ag tends to aggregate on Ag-Ru/SiO$_2$, this result suggests that it does block edge and defect-like sites to some extent, consistent with Monte Carlo simulations of Ag-Ru particles.[10] Prelimiary $^{13}$C data on Au-Ru/SiO$_2$ indicate that the hydrogenation capability is also reduced. This is a surprising result, since, of the three metals studied, Au has the least tendency to efficiently cover the Ru surface.

Conclusions.
　　Product distributions, reaction intermediates, and surface metal concentrations are very important clues in understanding the mechanistic details of heterogeneous catalytic reactions. This paper demonstrates the wealth of information available via solid state NMR, illustrated by the study of ethylene reaction on mono and bimetallic catalysts. On Ru/SiO$_2$, this reaction is a complex function of both temperature and exposure. For example, the evolution of weakly adsorbed C$_4$ species is observed only at higher exposures, whereas the strongly bound species tentatively identified as ethylidyne is only observed at low exposures. Hydrogenation reaction is extensive on Ru/SiO$_2$. The addition of Cu, Ag or Au to the catalyst generally reduces hydrogenation activity, presumably by the blockage of catalytically active edge and corner sites.

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